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PMMA - Impregnated Silica Gels: Synthesis and Characterization

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ABSTRACT

Shaped microporous silica has been prepared by a sol-gel process. The resulting silicas have 50% open porosity. The open porosity is filled by immersing the shapes in methyl methacrylate (MMA) and polymerizing with ultraviolet radiation. The fully impregnated silica is recovered in net shape.

The outstanding feature of the PMMA-impregnated silica is its transparency. There is little loss from scattering because of the nanometer scale of the microstructure and the similarity in index of refraction for silica and PMMA. The flexure strength of the silica-PMMA composite has been measured in 4-point bending. The strength increases at slower strain rates because the PMMA provides crack blunting. The composites can withstand thermal shocks up to about 150°C without losing strength. The thermal expansion coefficient for the range 0 to 150°C follows a mixing rule for 50% silica - 50% PMMA. While the mechanical behavior of the composite largely follows that of bulk PMMA, the microhardness is 3 to 5 times greater than for bulk PMMA.

1.0 INTRODUCTION

The sol-gel process has produced in recent years a number of interesting optical materials in both bulk¹ and fiber² form. The sol-gel process has also been used for optical waveguides on glass substrates.³ Another class of optical materials which uses the sol-gel process to prepare a microporous host is the class of gels doped with organic dyes. The organic molecules incorporated into gels include fluorescent dyes, laser dyes and non-linear optics. The inorganic hosts include alumina,⁴ titania-silica,⁵ aluminosilicates,⁶ zeolites,⁷ though primarily the host has been silica.^{8,9} In all of these cases, the host material needs to be transparent. In addition the host material must be environmentally stable.

It has been found that silica gels are environmentally stable when impregnated with PMMA (polymethyl methacrylate)^{10,11,12,13} and that the impregnated gels are also suitable hosts for organic molecules.^{9,14} In most of these studies,^{11,12,13} monolithic silica gels were infiltrated with MMA (monomer) following processing that involved catalysis with HF and firing to 800°C. After this treatment, the xerogels were 33% porous and had a median pore diameter of 10 nm. The porosity was infiltrated with monomer solution which polymerized in-situ. The resulting composites

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consisted of two fully percolating phases, a silica matrix and an organic polymer impregnant. Silica/PMMA composites were used to encapsulate electro-optically active organic compounds such as 2-methyl-4-nitroaniline (MNA). Electro-optical DC Kerr Effect and solid state deuteron NMR measurements were made.¹⁴ In a comparison to conventional optical cells, silica/PMMA composites were found to have better optical quality and retained dimensional stability to about 90°C. The composites were abrasion resistant and could be machined to complex shapes.

While the process described here is an interesting one for optical cells, it may also be a practical process for large scale windows once the process is simplified. When comparing sol-gel optics with conventional silica optics, the sol-gel process can hardly do better than duplicate the properties of conventional silica. However, when comparing silica/PMMA composites with bulk PMMA (PlexiglassTM), the composite can have better properties in terms of resistance to rain erosion, solvent crazing and weathering. Improvements in these properties have not been quantified, but qualitatively it is safe to say that the composites do not suffer from loss of transparency under conditions where PMMA does.

The objective of this study is to synthesize a silica/PMMA composite in the simplest way possible. Knowing that MMA readily adsorbs on acidic silica surfaces,¹⁵ even silica gels without high temperature treatment are expected to fill with MMA. Once silica/PMMA composites are fully impregnated and rigid, mechanical, thermal and optical properties can be evaluated and the environmental stability can be assessed.

2.0 SYNTHESIS

Silica gels were prepared from a solution of tetraethylorthosilicate (TEOS), distilled deionized water and ethanol. Equal volumes of distilled TEOS and ethanol were used. The molar ratio of water: TEOS was 16.¹⁶ The solution was catalyzed with 0.1 M HNO₃ and was stirred for 30 minutes. Ten ml of the solution were poured into polystyrene tubes and capped. The solutions gelled while in an oven for 7 days at 50°C, followed by 10 days at 70°C. The tubes then were uncapped and samples were dried in lots of 100 at 50°C for 14 days. Xerogels were removed from the tubes and dried 2 more days at 50°C. Finally, the gels were outgassed 24 hours at 250°C to remove physically adsorbed species.

A monomer solution of 1 g benzoyl peroxide (97%) catalyst per 100 ml MMA (methylmethacrylate, inhibited) was prepared (Aldrich Chemicals, Milwaukee, WI). After outgassing, each xerogel was immersed immediately in a borosilicate vial containing 11 ml of monomer solution (Figure 1a). The solution was allowed to infiltrate for 2 hours and then the sealed vials were subjected to 7 days of longwave UV illumination (Figure 1b) with a UV intensity of about 2000 micro W/cm². Once the PMMA was polymerized, the vials were cracked off and the PMMA surrounded silica gels were treated at 200°C in a mechanical convection oven for 30 minutes (Figure 1c). This is a temperature about 100° above the glass transition temperature of bulk PMMA and is also high enough to promote a moderate rate of depolymerization. This treatment turned the thick PMMA shell rubbery so that it could be peeled off by hand to recover net shape PMMA/silica gel composites (Figure 1d).

As Figure 1 is intended to show, the samples are roughly cylindrical. The diameter at the center of the composites is 5.60 mm and the length is about 33 mm.

According to nitrogen sorption analysis of the outgassed silica before infiltration, the surface area of the matrix is $900 \text{ m}^2/\text{g}$, and the porosity is almost completely microporous (less than 2.0 nm in diameter) and cylindrical in shape. The skeletal density is about 2.27 g/cm^3 , and the open porosity is 52.5%. Following infiltration and polymerization, the composite is close to theoretical density calculated by a mixing rule. The total weight gain during infiltration followed by polymerization is 50%. The density of the composite is 1.60 g/cm^3 .

3.0 TRANSPARENCY

Optical transmission was measured on a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer. Rods of outgassed silica xerogel, silica-PMMA composite, and PMMA of 10 mm length were cut or ground to length on a diamond saw, briefly hand ground dry on 600 grit abrasive paper, and polished with 1 micron diamond paste. Samples were mounted on a mask with a 4 mm aperture and the reference beam was obscured by a similar mask. Scan parameters included a slit width of 2 nm , a scan speed of 480 nm/min , and a response time of 0.5 sec . Automatic background correction was employed. The transmission curves were recorded and compared to see any changes in transparency.

The silica gel, PMMA and the composite were largely transparent over the range $380\text{--}800 \text{ nm}$. The transmission curves are shown in Figure 2. Transmission is highest in PMMA alone. Lower transmission is seen in the silica gel which may be the result of scattering from a few large pores. The transmission for the composite is nearly identical to the transmission for silica gel despite the difference in handbook values for index of refraction, 1.46 for silica and 1.49 for PMMA.

4.0 MECHANICAL PROPERTIES: STRENGTH AND MICROHARDNESS

Strength measurements were made by the four point flexure technique. The flexure fixture had a support span of 2.540 cm ($1.000''$) and a load span of 1.270 cm ($0.500''$). A gear driven Instron materials testing machine with a 1000 lb load cell was used. Crosshead speeds were between $.05 \text{ cm/min}$ ($0.02''/\text{min}$) and 5.08 cm/min ($2.0''/\text{min}$). A rapid strain rate was necessary to prevent plastic deformation in bulk PMMA. Composite samples were measured after exposure to ambient conditions. Water adsorption in composites corresponded to an increase in weight of 1.8% while in PMMA it was only on the order of $.1\%$. Sample test sets numbered 20 for silica/PMMA composites and PMMA.

Table 1 lists the strengths of silica-PMMA composites at the various strain rates. The distributions of Table 1 are illustrated in Figure 3. The strength distributions are represented by a two parameter Weibull analysis.¹⁷ At the highest strain rate estimated to be $3 \times 10^{-2}/\text{sec}$, composites had a mean strength of about 30 MPa . Upon decreasing the strain rate by one decade, to $3 \times 10^{-3}/\text{sec}$, the mean strength increased to about 100 MPa . Strength then remained about the same as strain rate was twice again decreased by one decade. The dramatic increase in flexure strength upon decrease of strain rate from $3 \times 10^{-2}/\text{sec}$ to $3 \times 10^{-3}/\text{sec}$, likely is due to the "brittle-ductile" transition of the polymer phase.¹⁸ In polymers, both brittle and ductile fracture involve plastic deformation. In thermoplastics such as PMMA, brittle fracture is characterized by localized crazing and localized volume increase. Ductile behavior is characterized by constant volume

shear yielding in the bulk and also by crack tip blunting. The brittle and ductile mechanisms are competitive but not mutually exclusive.

The apparent brittle-ductile transition of the silica-PMMA composite results in higher strength for the composites at low and moderate strain rates. The reason for this may be crack blunting and shear yielding of the PMMA, which reduces the stress at the crack tip, thereby increasing flexure strength. In comparison, pure PMMA had a mean strength of about 120 MPa when PMMA was measured at the highest strain rate. At this strain rate of 3×10^{-2} /sec, bulk plastic deformation was avoided. However, PMMA rods fractured at a strain rate of 3×10^{-4} /sec were observed to be permanently bent. The strengthening mechanism for the PMMA in the composite is no longer evident when strengths were measured at 400°C. Apparently, the decrease in stiffness of the MMA at elevated temperature diminishes its ability to provide crack blunting.

Vickers hardness was measured on a Zwick 3212.00 hardness tester. Test parameters included an impact speed of 0.3 mm/sec, an indent time of 30 sec, and a load of 1.0 kg. All samples were left in rod shape and were rested on a V-block. The values as determined by the Zwick computer were corrected for cylindrical surfaces. The number of samples per test was 10 and each sample was indented once.

Table 2 summarizes the results of hardness tests. Bulk PMMA exhibited the lowest hardness. Porous xerogels were more than twice as hard as PMMA. The silica-PMMA composites were by far the hardest.

Table 1: Strengths of Silica-PMMA Composites vs Strain Rate

Strain Rate (sec ⁻¹)	Strength (MPa)	Weibull Parameter	
		m	R ²
3 x 10 ⁻²	34 +/- 2	3.2	.94
3 x 10 ⁻³	96 +/- 5	4.6	.95
3 x 10 ⁻⁴	99 +/- 5	4.7	.96
3 x 10 ⁻⁵	93 +/- 5	4.4	.97

Table 2: Vicker's Hardness

Material	Vicker's Hardness (MPa)
PMMA	152 +/- 1
Silica Xerogel, exposed	355 +/- 3
Silica Xerogel, fresh	413 +/- 2
Silica-PMMA composite, exposed	881 +/- 11
Silica-PMMA composite, fresh	988 +/- 8

5.0 THERMOMECHANICAL PROPERTIES: THERMAL SHOCK AND THERMAL EXPANSION

The resistance of PMMA-silica composites to thermal shock damage was evaluated qualitatively and quantitatively. Samples were heated in a mechanical convection oven and then quenched in ice-water to give shocks corresponding to between 75 and 200°C. The frequency of damage visible to the naked eye was then recorded and flexure strength was measured at a crosshead speed of 0.0508 cm/min (0.02"/min). Damage was observed with the unaided eye at a temperature difference of 90°C or greater. At a temperature difference of 150°C and above, all samples appeared damaged. The damage was in the form of cracks that extended throughout the bulk of the sample. The number of cracks observed increased with increasing temperature difference, though all samples retained their overall shape. The mean flexure strengths for each set of 5 samples is plotted on Figure 4 vs temperature difference. Strength dropped sharply for a temperature difference of 150°C or greater. In total, 24 of the 50 samples survived the ice water quench test without visible damage.

Thermal analysis was performed on the Perkin-Elmer Series 7 Thermal Analysis System. A heating rate of 10°C was used in all tests and temperature was varied from -25 to 200°C. Coefficient of thermal expansion was calculated by the Perkin-Elmer software. Thermal mechanical analysis in flowing helium was performed on 7 mm long rods of silica-PMMA composite. A probe load of 100 mN was used.

The trace is shown in Figure 5. The mean thermal expansion coefficient is $3.6 \times 10^{-5}/^{\circ}\text{C}$, where the expansion coefficient for bulk silica is 5×10^{-7} and that for bulk PMMA is 7×10^{-5} . The composite was cycled without any apparent damage.

6.0 SUMMARY

In summary, the synthesis of silica-PMMA composites has been simplified and carried out in large quantities. The benefit of the PMMA impregnant on the silica xerogel is to render it less sensitive to moisture. The improvement of environmental stability by PMMA impregnation is quite evident even before intentional application of stress. While porous xerogels typically exhibit limited shelf life due to the stresses caused by adsorption and desorption of water, composites in the open remain intact even after years of exposure. Only composites that are intentionally scratched exhibit a shelf life short enough to be observed.

The mechanical properties, flexure strengths and hardness have been evaluated. Overall, the mechanical behavior of the composite is more like that of bulk PMMA than bulk silica except that the hardness is much higher than bulk PMMA. The thermomechanical properties have been evaluated. Despite a large thermal expansion mismatch, the composite expanded and contracted without disruption. The maximum exposure temperature for the composite is recommended to be no higher than about 100°C for extended periods of time. Preferably, the composite would only see service at room temperature to -50°C. Finally, the composite material is transparent in the visible range so its use as a window is conceivable.

7.0 ACKNOWLEDGEMENT

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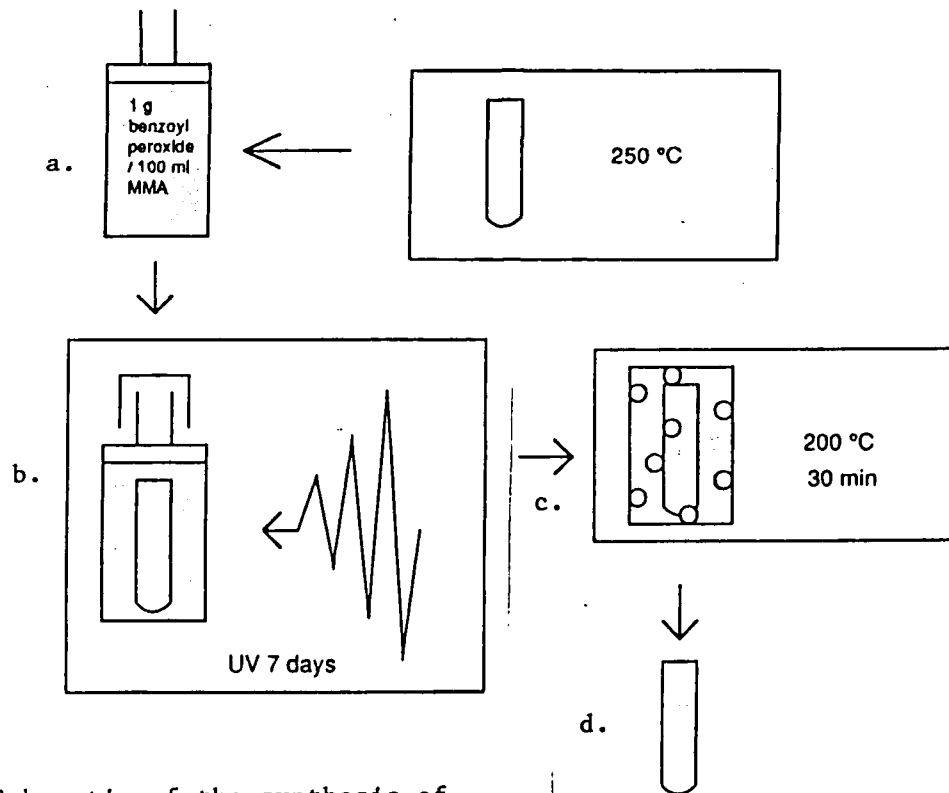


Figure 1: Schematic of the synthesis of silica/PMMA composites

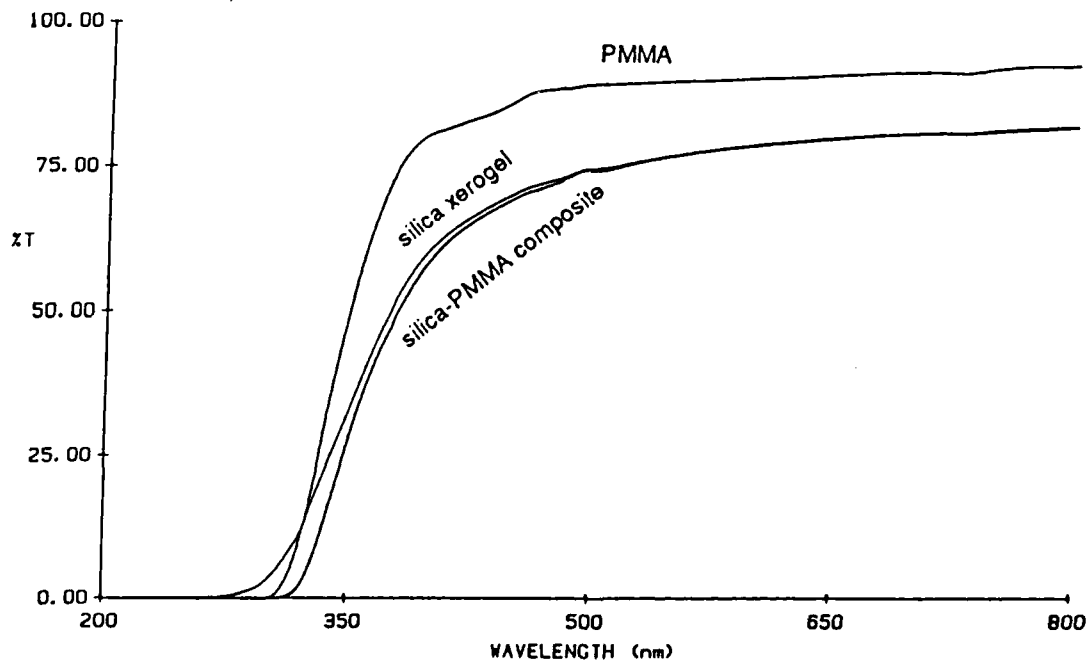


Figure 2: Percent of incident radiation transmitted for 10 mm thick samples

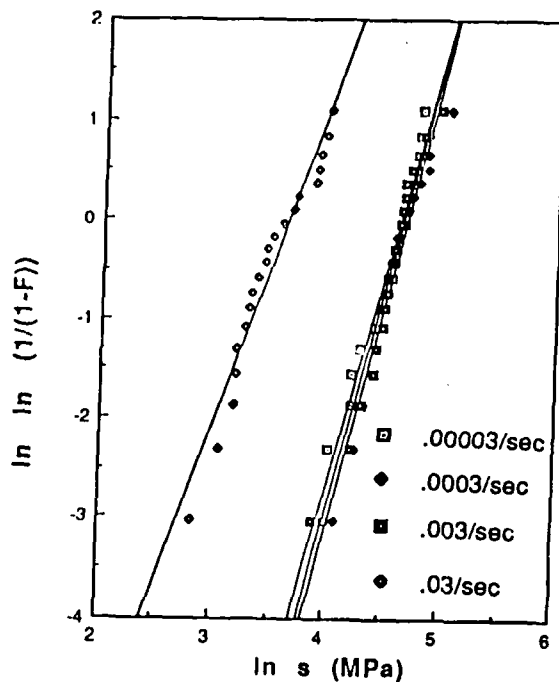


Figure 3: Strength distributions for 4 strain rates in silica/PMMA composites

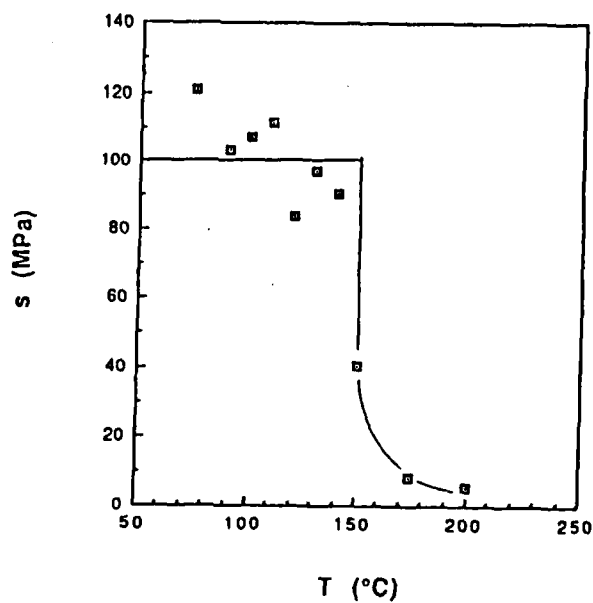


Figure 4: Flexure strength of samples after being subjected to thermal shock

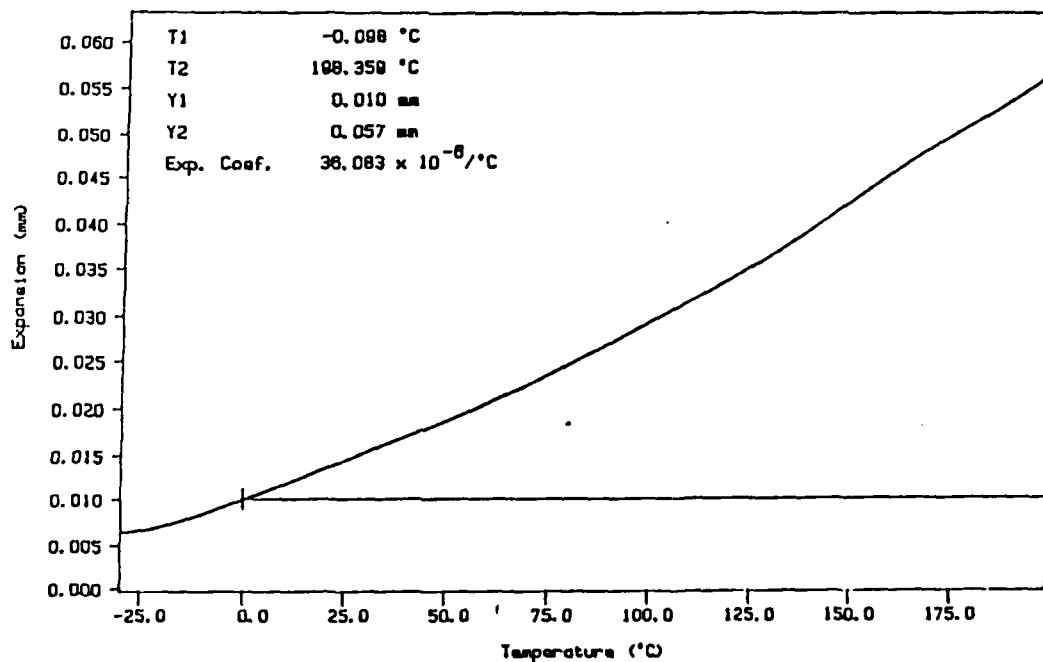


Figure 5: Thermomechanical analysis used to determine thermal expansion coefficient for silica/PMMA composite over the range 0 to 200°C